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ABSTRACTS

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(Pages refer to the Japanese originals of this volume unless otherwise noted.)

Enzymatic Studies on Exuvial Fluid of Bombyx Mori L. (Silkworm)

(pp. 905~909)

Part I. Detection of the Enzymes in the Exuvial Fluid.

By Yasuji HAMAMURA, Senji IIDA and Minoru OTUKA.

(Kyoto Kōtō Sansi Gakkō; Received August 15, 1940.)

We found protease, invertase and amylase in the exuvial fluid of silkworms and did not find lipase and tyrosinase. The exuvial fluid has hitherto been believed to exert only mechanical action at moulting, but our detection of enzymes therein suggests that the exuvial fluid acts not only mechanically but also enzymatically on an inner part of the old skin of silkworm at moulting.

Part II. On the Chitinase.

By Yasuji HAMAMURA and Yasusuke KANEHARA.

We found chitinase in the exuvial fluid and glucosamine in the water extract of the exuvia of silkworm. This fact shows that the chitinase in exuvial fluid acts on the chitin material of the exuvia at moulting.

The optimum pH of the chitinase action was found to be 8.2 and the optimum temperature 50°C.

Zur Kenntnis von 6-Nitro-derivaten des Sterins.

(Zuckerrohrwachs. VI. Mitteilung.)

(SS. 910~916)

Von T. MITUI.

(Aus d. Agrikulturchem. Laboratorium der Kaiserl. Universität Kyoto;

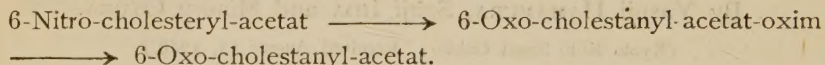
Eingegangen am 18. 8. 1940.)

Reduktion von 6-Nitro-steroid.

Nach Windaus⁽¹⁾ wird 6-Nitro-cholesteryl-acetat mittels Zinkstaub und Eisessig unmittelbar in 6-Oxo-cholestanyl-acetat reduziert.

Es ist dem Verf. gelungen, das Zwischenprodukt dieser Reaktion zu erhalten. Durch Behandlung mit Zinkstaub und Äther-Eisessig (1:1) eragab 6-Nitro-cholesteryl-acetat eine Substanz vom Schmp. 199°, die bei weiterer Reduktion mit Zinkstaub und Eisessig in 6-Oxo-cholestanyl-acetat (Schmp. 128°; *p*-Nitro-phenylhydrazon: Schmp. 145°) übergeführt wurde.

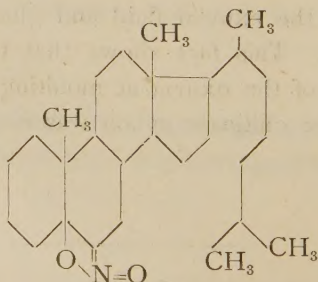
Aus 6-Oxo-cholestanyl-acetat wurde mit Hydroxylamin sein Oxim hergestellt, das bei 200° schmolz und mit dem oben gewonnenen Zwischenprodukt identisch war. Nun ist es klar geworden, daß die Reaktion wie folgt verlaufen ist.



Bei der Reduktion des 6-Nitro-sitosteryl-acetats sowie des 6-Nitro-stigmasteryl-acetats wurde ganz analog als Zwischenprodukt das Oxim des 6-Oxo-sitostanyl-acetats (Schmp. 136°) bzw. des 6-Oxo-stigmastanyl-acetats (Schmp. 172°) erhalten.

Isomerisieren von 6-Nitro-steroid mittels Alkali.

Wenn man 6-Nitro-cholesten mit 5% Methanol-KOH oder 5% Na-Methylat behandelt, so geht es in eine alkalilösliche Substanz über. Der beim Ansäuern des Reaktionsgemisches auftretende Niederschlag wurde aus Methanol umkrystallisiert, dabei schied sich eine Substanz vom Schmp. 113° aus. Die Analyse dieser Substanz erbringt die Formel $C_{27}H_{45}O_2N$, ist also ein Isomer des Ausgangsstoffes. Ihren Eigenschaften nach muß sie die folgende Struktur besitzen.



Dieselbe Substanz kann man aus 3-Chlor-6-nitro-cholesten durch die gleiche Behandlung gewinnen.

Aus 6-Nitro-cholesteryl-acetat sowie aus 6-Nitro-cholesteryl-propionat durch Alkali-Behandlung wurde eine analoge Substanz vom Schmp. 152° erhalten, deren Derivate sind:

Acetat	Schmp.	96.5°	$C_{29}H_{47}O_2N$
Benzoat	Schmp.	175°	$C_{34}H_{49}O_4N$
<i>m</i> -Dinitro-benzoat	Schmp.	158°	$C_{34}H_{47}O_6N_3$

Aus 6-Nitro-stigmasteryl-acetat durch Alkali-Behandlung wurde die Substanz vom Schmp. $91\sim 93^{\circ}$ gewonnen.

Schrifttum.

Windaus: Ber, **36**, 3754 (1903).

Oxydationsversuche mit Zuckerrohrsitosterin II.

(Zuckerrohrwachs. VII. Mitteilung.)

(SS. 917~492)

Von T. MITUI.

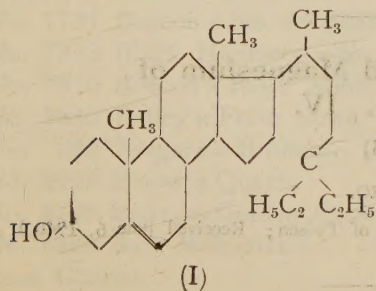
(Aus d. Agrikulturchem. Laboratorium der Kaiserl. Universität Kyoto;

Eingegangen am 18. 8. 1940.)

Wie in der II. Mitteilung berichtet wurde, hat der Verf. aus dem Oxydationsprodukt des Zuckerrohrsitosteryl-acetat-dibromids ein neues "Oxyketon" (Schmp. 114°) gewonnen. Nach weiteren Untersuchungen konnte er seine Struktur sicher stellen.

Durch die Clemmensen-Reduktion des Oxyketons hat der Verf. eine Oxyverbindung vom Schmp. 132° (Acetat: Schmp. 120°) gewonnen und als 3-Oxy-nor-sitosten angenommen. Inzwischen hat er 3-Oxy-nor-sitosten aus 3-Oxy-cholensäure auf folgende Weise synthetisiert.

3-Oxy- Δ^5 -cholensäure \rightarrow 3-Acetoxy-cholensäure-methylester — Diäthyl-Mg-J \rightarrow 3-Oxy-cholensäure-diäthyl-carbinol (Schmp. $160\sim 163^{\circ}$; Dichlorid: Schmp. $116^{\circ} \rightarrow$ Nor-sitosten: Schmp. $66\sim 67^{\circ}$) — Essiganhydrid bei $0^{\circ} \rightarrow$ 3-Acetoxy-cholensäure-diäthyl-carbinol (Schmp. 129.5° — Essiganhydrid bei $100^{\circ} \rightarrow$ 3-Acetoxy- $\Delta^5, 6; 23, 24$ -nor-sitostadien: Schmp. 117°) — Thionylchlorid \rightarrow 3-Acetoxy-cholensäure-diäthyl-carbinol-chlorid (Schmp. 130.5°) — Na-*n*-Propylat \rightarrow 3-Oxy-nor-sitosten (I) (Schmp. 134.5° ; Acetat: Schmp. 137°)

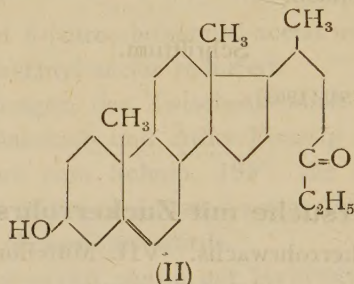


— Pt $O_2 + 1$ Mol $H_2 \rightarrow$ 3-Oxy-nor-sitostan
(Schmp. $131\sim 132^{\circ}$; Acetat: Schmp. 131°)

Beim Vergleich dieses synth. 3-Oxy-nor-sitosten mit dem Reduktionsprodukt des Oxyketons ergab sich, daß die beiden Substanzen nicht identisch sind.

Hiermit wurde 3-Oxy-nor-cholesten-24-on und sein Derivat aus 3-Oxy-choleensäure hergestellt.

3-Acetoxy-choleensäure $\xrightarrow{\text{Thionylchlorid}}$ 3-Acetoxy-choleensäure-chlorid $\xrightarrow{\text{NH}_4\text{OH}}$ 3-Acetoxy-choleensäure-amid (Schmp. 210~212°) $\xrightarrow{\text{Diäthyl} \cdot \text{Mg} \cdot \text{J}}$ 3-Oxy-nor-choles'en-24-on (II) (Schmp. 114° bei 90° sint.; Acetat: Schmp. 167~168°) $\xrightarrow{\text{Clemmensen-Reduktion}}$ 3-Oxy-nor-cholesten (Schmp. 132°; Acetat: 120°)



Durch eine Mischschmelzprobe dieses synth. 3-Oxy-nor-cholesten-24-ons mit dem oben erwähnten neuen Oxyketon konnte ihre Identität bestätigt werden. Weiter wurde 3-Oxy-nor-cholesten durch die Clemmensen-Reduktion des synth. 3-Oxy-nor-cholesten-24-ons erhalten, das auch mit dem Reduktionsprodukt des aus Sitosteryl-acetat-dibromids erhaltenen neuen Oxyketons identifiziert wurde. Dieses 3-Oxy-nor-cholesten wurde auch noch aus 3-Oxy-nor-cholesten-25-on durch die Clemmensen-Reduktion erhalten.

Auf Grund dieser Ergebnisse wurde festgestellt, daß die Struktur des neuen Oxyketons vom Schmp. 114.5° zweifellos 3-Oxy-nor-cholesten-24-on (II) ist.

The Physiological and Chemical Function of Potassium in Plants, with Special Reference to the Behavior of Potassium in Growth and Maturity.

(pp. 925~938)

By Kisaburo SHIBUYA and Takashi TORII.

(Taihoku Imperial University; Received August 7, 1940.)

Exchangeable Calcium and Magnesium of Soils in Tyōsen. IV.

(pp. 933~948)

By MISU-HIDEO.

(Agricultural Experiment Station, Government General of Tyōsen; Received June 6, 1940.)

On the Selection of Grape Varieties for Wine Making. (Part 3.)

(pp. 949~962)

By Zenbei KAWAKAMI and Takasi HUKINBARA.

(Iwanohara Vineyard; Received August 26, 1940.)

The present study is the continuation of previous work reported by H. Kawakami and S. Masumiya and Z. Kawakami and T. Hasegawa.

The grapes used in the present experiments are known varieties and crosses of European and American origin besides new crosses obtained by Z. Kawakami in Iwanohara vineyard, Niigata Prefecture. They are as follows:—

a) Twenty-six known varieties of foreign and three Japanese native varieties are as follows:—

Hartford.	Campbell Early.	Unknown Spec. No. 3.
Big Extra.	Telegraph.	Cottage.
Zinfandel.	Cot à que Verte.	Carman.
Bailey.	Beacon.	Ives.
W. B. Munson.	Mills.	Concord.
Hybrid France.	Aomori and Siburo native grapes.	Jack.
Mataro.	Merlot.	Muscat Hamberg.
Herbemont.	Unknown Spec. No. 1.	Niagara.
Perry.	Chasselas De Fontainebleau.	Gold Queen.
Sanjyaku.	Kōsū.	

b) Thirty-five Z. Kawakami's new crosses are as follows:—

No. 3 Big Extra.	No. 7 Extra Folle.
No. 55 Bailey Alicante A.	No. 56 Bailey Alicante B.
No. 69 Beacon Alicante.	No. 1 Bailey × Zinfandel.
No. 2682 Campbell Early × Highland.	No. 3986 Muscat Bailey A.
No. 4021 Bailey × Muscat Hamberg.	No. 4031 Muscat Bailey B.
No. 4083 Bailey × Muscat Hamberg.	No. 4131 Black Queen.
No. 4176 Bailey × Chasselas Ciutat.	No. 4183 Bailey × Muscat Hamberg.
No. 5778 Adirondack × No. 7 Extra Folle.	
No. 5788 Adirondack × No. 7 Extra Folle.	
No. 7709 Campbell Early × No. 7 Extra Folle.	
No. 7431 Carman Alicante.	No. 7788 Beacon × No. 56 Bailey Alicante B.
No. 7791 Beacon × No. 56 Bailey Alicante B.	
No. 7852 Black Hamberg × No. 56 Bailey Alicante B.	
No. 7875 Beacon × Folle Noire.	No. 7879 Bailey × Folle Noire.
No. 7882 Bailey × Folle Noire.	No. 7889 Bailey Alicante B × Beacon.
No. 385 Niagara × Brilliant.	No. 413 Rose Queen.
No. 4123 Bailey × Queen.	No. 4123 Gold Queen.
No. 4126 Bailey × Golden Queen.	No. 4600 Verdelho × Golden Chasselas.
No. 6421 Red Millennium.	No. 6952 Lady Washington × Sanjyaku.
Rose Ciutat.	White Bailey.

Z. Kawakami's new crosses are generally better than the existing varieties in colour, but require more investigation as to taste and fragrance.

(1) H. Kawakami and S. Masumiya: This Jour., **14**, 1437 (1938).

(2) Z. Kawakami and T. Hasegawa: This Jour., **15**, 1149 (1939).

On Ascorbic Acid Formation in Plant and Animal Bodies. VI.

(pp. 963~964)

By Tetutaro TADOKORO and Masao NISIDA.

(Hokkaido Imperial University; Received September 5, 1940.)

Experimentelle Untersuchungen über die Wirkung von Radium und Röntgenstrahlen auf die Gärungsmikroorganismen.

(SS. 965~978)

Von Mituo SIMO.

(The Institute of Research on Chemical Industry, Government-General of Taiwan;

Received September 16, 1940.)

On the Pentose-fermenting Lactic Acid Bacteria.

(pp. 979~984)

By Mamoru IWASAKI.

(Agricultural Chemical Laboratory, Tokyo Imperial University;

Received Sept. 12, 1940.)

Two new varieties of lactic acid bacteria, which ferment xylose vigorously, forming lactic and acetic acids in the yields of 85~96% against the pentose used, were isolated. The ratio between the quantities of both acids produced was lactic: acetic=58~59:41~42. Various conditions for the industrial application of the fermentation were studied. The bacteria were classified as follows:

Lactobacillus pentoaceticus var. *magnus*, nov. var.

Rods: Slender, 0.7~0.9 by 3~4 microns, occurring singly or in pairs. Non-motile. Spore not formed. Gram positive.

Broth: Carbohydrates necessary for growth. Bouillon or yeast extract: scanty. Wort or Koji-extract: Turbid within 2 days. Clears with somewhat slimy sediment and thin pericle.

Gelatin: No liquefaction. Koji-extract or wort gelatin stab: Abundant development in stab and slight surface growth. Gas formation.

Agar: Koji-extract or wort agar slant: Narrow, whitish, somewhat translucent.

Litmus milk: Acid, without coagulation.

Nitrite reduction: negative.

Catalase not produced.

Temperature relations: Opt. for growth, 33~35°C. Opt. for acid formation, 31~33°C. Killed in 10 minutes at 65°C.

Acid formed from xylose, arabinose and fructose vigorously; from glucose, galactose and maltose moderately; from raffinose, mannose and lactose feebly. Saccharose, inulin and mannitol not fermented. Abundant volatile acid formed from xylose, arabinose and fructose.

Gas from fructose, glucose, mannose, galactose, raffinose and maltose. No or slight (if any) gas formation from arabinose and xylose.

Inactive lactic acid and acetic acid formed from xylose in the proportions of 58~59:41~42, and with the yields of 85~93% against the sugar consumed.

Mannitol formed from fructose.

Microaerophilic.

Source: Isolated from *Colocasia antiquorum*, Schott.

Lactobacillus mannitopoeus var. *fermentus*, nov. var.

Rods: Short, 0.6~0.7 by 1.2~1.5 microns, occurring sometimes singly, but mostly in pairs or chains. Non-motile. Spore not formed. Gram positive.

Broth: Carbohydrates necessary for growth. Bouillon or yeast extract: scanty. Koji extract or wort: Turbid with thin pericle and heavy sediment.

Gelatin: Not liquefied. Koji extract or wort gelatin stab: Good growth on surface as well as in stab. Gas formed.

Agar: Koji extract or wort agar: Filiform, milky white, somewhat shining.

Litmus milk: acid, without coagulation.

Nitrite reduction: negative.

Catalase not produced.

Temperature relations: Optimums for growth, 31~33°C; for acid formation, 28°C. Killed in 10 minutes at 60°C.

Acid formed from arabinose and xylose abundantly, from glucose, fructose, mannose, raffinose, saccharose, maltose, galactose, lactose and α -methyl-glucoside moderately. Abundant volatile acid from arabinose, xylose and lactose. Inulin and mannitol not fermented.

Abundant gas from fructose, glucose, raffinose, saccharose and maltose. No or slight (if any) gas from pentoses.

Inactive lactic acid and acetic acid formed from xylose in the proportion of 59:41, and with the yields of 90~96% against the sugar consumed.

Microaerophilic.

Source: Isolated from the fermented mash of Shao-hsing-chiu.

Studies on the Production of Acetone and Buthanol by Fermentation.

(pp. 985~1006)

By Sinji Dori and Takeo YAMADA.

(Agricultural Chemical Laboratory, Tokyo Imperial University;

Received September 13, 1940.)

On the Chemical Composition of Loquat.

(pp. 1007~1011)

By Tasuku HIBINO.

(Chemical Laboratory, Hirosima Higher School; Received September 16, 1940.)

On the Production of 2,3-Butylene Glycol by Fermentation. A Supplement to Part I.

(A Method for the Industrial Utilization of Pentose).

(pp. 1012~1014)

By Kin-ichirô SAKAGUCHI, Mareyuki OHARA and Susumu KIKUTI.

(Agricultural Chemical Laboratory, Tokyo Imperial University;

Received September 6, 1940.)

In the previous paper the authors reported that 2,3-butyleneglycol could be prepared technically through the fermentation process by the use of several strains of bacteria isolated by them. Saccharose, fructose and xylose have been used as raw materials in the present work. The yields of the glycol and ethyl alcohol against the sugars consumed have been found to be as follows:

Sugars used	The yields of		Sugars used	The yields of	
	Butylene glycol	Ethyl alcohol		Butylene glycol	Ethyl alcohol
Xylose a	27.03%	15.65%	Fructose	21.57%	10.92%
b	25.73	12.31	Saccharose	25.27	9.34
c	27.40	14.65	Glucose	29.51	12.23

From the results shown above, it is obvious that those sugars can also serve as raw materials for the production of the glycol. Various quantities of ethyl alcohol to the extent of about one half of these of the glycol are obtained as by-product.